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# Modification of Silver Nanoparticles in Homogeneous Solutions

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# MODIFICATIONS OF SILVER NANOPARTICLES IN HOMOGENEOUS SOLUTIONS

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A Thesis  
Presented to  
the Graduate School of  
Clemson University

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In Partial Fulfillment  
of the Requirements for the Degree  
Master of Science  
Chemistry

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by  
Dallas Ann Roe Estepp  
August 2017

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Accepted by:  
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## ABSTRACT

Silver nanoparticles (AgNP) are used for many analytical and imaging techniques because they represent the most efficient mechanism by which light interacts with matter. The stability of AgNPs remains an important factor for their application. Due to their tendency to aggregate, methods for stabilizing AgNPs, mainly the addition of surfactants, have been developed. Surfactants can prevent agglomeration of AgNPs, however they can inhibit further surface modification of the particles. To overcome this problem, AgNPs were synthesized in the presence of  $\text{Na}_2\text{SiO}_3$ , yielding a silica shell that substantially improved the particles' stability without compromising their surface chemistry. Potential benefits are described in chapter 1. Details of this method allowing controlled thickness of a silica shell via ethanol precipitation are presented in chapter 2. These silica shells can act as a scaffold for further surface modification as well as allow the synthesis of asymmetric structures. To prove the concept of the asymmetric structure synthesis, silver dimers were synthesized by impregnating the silica shell with silver ions. Uniform dimers were made via a homogeneous solution reaction. The method is expected to find general applicability for synthesizing various oligomeric nanostructures.

In chapter 4, shape change via partial dissolution of crystalline AgNPs in aqueous suspension are discussed. The dissolution of particles yielded more rounded crystals contain many small facets which are more reactivity than the large facets of the initial crystalline state. This finding opened the possibility for producing more reactive nanoparticles. That can find applications such as Surface Enhanced Raman Scattering as well as catalysis are expected to be improved upon using this more reactive crystalline form of AgNP.

## DEDICATION

I dedicate this thesis to my family and friends. I could not have made it this far without their love and support.

## ACKNOWLEDGEMENTS

First I would like to acknowledge my advisor, Dr. George Chumanov, for his support throughout my time in this lab. With his guidance and knowledge, I have been able to become a better scientist. I would also like to acknowledge my past and present group members for their help and support. I would like to thank Clemson University and my committee members for the opportunity to learn and grow as a chemist.

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## CHAPTER ONE

### INTRODUCTION

Synthesis of metallic nanoparticles has been a growing field due to their potential wide applicability. Applications include catalysis<sup>1,2</sup>, optics<sup>3</sup>, sensing<sup>4,5</sup> and multifunctional core-shell composites<sup>6,7,8,9</sup>. Silver nanoparticles (AgNPs) represent the most efficient mechanism, by which light interacts with matter due to the excitation of plasmon resonances.<sup>10,11</sup> An important property of AgNP is that their plasmon resonance frequency can be tuned across the visible and near infrared spectral range. Plasmon resonances are collective oscillations of conduction electrons. The tunability of the plasmon resonance gives silver based nanomaterial a unique flexibility towards the design of optical applications.<sup>3,11</sup>

Like many other metallic nanoparticles, AgNPs in suspension have a tendency to aggregate. Most AgNPs are made with capping agents such as surfactants to prevent the particles from aggregation.<sup>10</sup> Many of these capping agents cause unwanted reactions, limit the growth of particles as well as interfere with particle surface modification. Silica coating of the particle is viewed as a better alternative to organic capping agents.<sup>6</sup> Silica was chosen to protect the AgNPs because it is optically transparent and does not dampen the plasmon resonance, and can be made very thin so

that the particle's local electromagnetic field is still extending beyond this silica shell for sensing applications.<sup>12</sup> There are many reported methods for attaching silica to AgNPs but two main methods are at the core of the different adaptations. These methods are the Stober method<sup>13</sup> and a method developed by Mulvaney *et al.*<sup>6</sup> The Stober method uses a silica precursor, tetraethyl orthosilicate (TEOS), which forms a silica shell via hydrolysis and condensation reactions.<sup>13</sup> The method developed by Mulvaney *et al.* utilizes 3-aminopropyl-trimethoxysilane (APTES) to attach to the surface of the metallic nanoparticle creating a vitreophilic surface. Then sodium silicate is added at supersaturated concentrations, resulting in a monolayer of silica on the surface. Finally, ethanol is added to precipitate the remaining silica onto the surface of the particle producing a thicker shell.<sup>6</sup> In our lab, a method was developed in which sodium silicate together with Ag<sub>2</sub>O in water was subjected to the hydrogen reduction process. As the reaction proceeds AgNPs are formed together with a thin silica shell; the porosity of a silica shell allows further growth of the nanoparticles to any desired size. The resulting particles feature an ultra-thin silica shell of approximately 1- 2nm thick.<sup>14</sup>

The ultra-thin silica shells are not uniform across the surface of the AgNPs. These shells are good for long periods of storage of the AgNPs but are not thick enough to use as a scaffold for surface modifications without

risking aggregation. Moreover, observations of shape change in the ultra-thin silica shell AgNPs have been observed when the particles were diluted with water. These results lead to the hypothesis that a thicker shell will fully stabilize the AgNPs which can be made by ethanol precipitation of sodium silica. From this hypothesis a method was development of controlled fabrication of various thickness of silica shell around AgNPs that are stable and can be modified without aggregation. In addition, the silica shell on the AgNP allows the fabrication of multifunctional nanoparticles via the formation of oligomeric nanoparticles with difference chemical/optical properties. As an example of this general approach, AgNPs with relatively thick silica shell were impregnated with additional silver ions. The hydrogen reduction reaction resulted in the uniform formation of silver dimers. The ability to uniformly synthesize dimers in the bulk via homogeneous solution reactions is an important advantage of this approach. Contrary, in reported methods dimers and other desired oligomeric structures comprise only a fraction of the total nanoparticle population.

## CHAPTER TWO

### THICK SILICA SHELL USED AS STABILIZER, MADE VIA ETHANOL PRECIPITATION

#### Introduction

Aggregation is the main issue in the nanoparticle field. When suspensions are not stabilized, particles stick together. Aggregation is often an irreversible process. To combat this issue many different stabilizers have been made to keep the particles in suspension and to prevent aggregation. Surfactants such as cetrimonium bromide (CTAB) have been used to stabilize particles by lowering the surface energy.<sup>15</sup> While aggregation is prevented, the stabilizers make modifications to the particles difficult due to surface blocking and potential secondary reactions.

Laying the ground for this project, our group has previously used silica to stabilize the AgNPs. Silica is easy to use and inert in terms of reactivity with silver. Various different methods have been used to attach silica to the surface of the AgNPs. The current method which has been employed makes an ultra-thin silica shell in a simple addition process.<sup>14</sup> The addition of sodium silicate to our standard hydrogen reduction of silver method creates a thin layer of silica on the particle which prevents aggregation during long periods of storage.<sup>14</sup> This ultra-thin shell is not

uniform, containing holes that negatively affect particle stability especially when surface modifications are tempted. To strengthen this shell, more silica was added to the surface of the AgNPs via ethanol precipitation. This is a simple method permitting the synthesis of shell of any desired thick as well as providing a scaffold for further surface modification to the AgNPs without aggregation.

### Materials and Methods

Materials: Silver (I) oxide (99.99%) was purchased from Alfa Aesar. Sodium Metasilicate ( $\text{SiO}_2$  44-47%) and 160000 MW Poly(4-vinylpyridine) (PVP) were purchased from Sigma-Aldrich. Ultra high purity hydrogen was purchased from Air Gas. Deionized water with a normal resistivity of  $18\text{M}\Omega\cdot\text{cm}$  was obtained from a Millipore Milli-Q water purification system. USP/ACS grade absolute 200 proof ethanol was obtained from Aaper Alcohol & Chemical Company. Indium tin oxide (ITO) glass ( $8\text{-}12\Omega/\text{sq inch}$ ) was purchased from Sigma and Delta Technologies, LTD. Conductive Silver paint was purchased from PELCO®.

Instrumentation: A Shimadzu UV-2501 PC spectrometer was used to record all UV-vis spectra. A Hitachi SEM-4800 was used to take scanning electron microscopy (SEM) images.



Methods: AgNPs were made by hydrogen reduction which is a technique previously developed by our lab. These AgNPs contain an ultra-thin silica shell due to the addition of 50-250 $\mu$ M Na<sub>2</sub>SiO<sub>3</sub> (47%) at the start of the reaction. After synthesis, the AgNPs were filtered to remove excess Ag<sub>2</sub>O. A Nylon membrane of 0.22 microns was used to filter the particles. Then the AgNPs were concentrated by using the centrifuge at 1000rpm for approximately 1.5 hours. The AgNPs were added to a solution of 1mM Na<sub>2</sub>SiO<sub>3</sub>. A duplicate of AgNPs containing no silica was made for comparison and was recorded by the UV-vis spectrometer. Ethanol was added to both solutions dropwise, to prevent aggregation of the particles, until the solution reached 80% ethanol. Spectra of the solutions were recorded by the UV-vis spectrometer to distinguish the shift due to ethanol and the shift due to condensation of the silica shell.

To view the silica shell, Scanning Electron Microscope (SEM) images were taken of the AgNPs. The SEM software was used to determine size of the particles as well. The ITO glass substrate which was used for imaging was modified using 0.25% PVP by rolling the glass in solution overnight. The slides were rinsed with ethanol four times and DI water two times. 20 $\mu$ L of AgNPs was dropped onto the slide in a 100% humidity box and allowed to slowly adhere to the surface of the PVP modified glass. The box was a glass box containing glass vials filled with sand. Water was added until

approximately half of the vial was submersed. The slides were placed on top of the vials and the lid was closed. This box was used to prevent drying of the AgNPs which would cause aggregation. The slides stayed in the box overnight and were dried with nitrogen gas the next day. As a precaution, the slides were placed in the oven at 140°C for approximately 30 seconds to ensure all liquid was gone. This same procedure was used for all SEM images.

### Results and Discussion

The condensation of the silica on the surface of the AgNPs was monitored by the spectral shifts of the plasmon resonance as monitored by UV-vis spectroscopy. Spectral shifts of the plasmon resonance are due to the change in the resonance frequency of the oscillating electrons within the particle. When the incident light hits the particle at the resonance frequency, the electrons begin to oscillate. This oscillation creates a local electromagnetic field which causes induced polarization in the outside medium. The restoring force causes a retardation in the oscillation which is manifested as a delay. This delay shifts the resonance to a lower frequency which is monitored as a shift to longer wavelengths.<sup>3</sup> For the experiment, shown in figure 2.1, an initial spectrum was taken of the solution containing AgNPs before the addition of the silica precursor. Then a spectrum was

recorded after the addition of 1 mM  $\text{Na}_2\text{SiO}_3$ . This spectrum showed a shift to longer wavelengths (or red shift) of approximately 5 nm in the quadrupole and 3 nm in the dipole with respect to the control experiment. The broad peak around 540 nm and a peak at 420 nm belongs to dipole and quadrupole electron oscillation modes respectively.<sup>10,18</sup> It is reasonable to assume that some silica spontaneously goes onto the surface of the AgNPs due to the affinity to the already present ultra-thin shell on the particles. This initial red shift is larger for the quadrupole mode because the local field associated with this mode is more localized on the surface of the particles.<sup>18</sup> Therefore the addition of a small amount of silica that increases the local dielectric function affects the quadrupole more than dipole frequency. Once the ethanol was added, a larger red shift occurred in the dipole mode due to the combination of ethanol and condensation of more silica. The duplicate AgNPs containing no silica were used to determine the shift due to the ethanol only. The dipole shift is larger because the quadrupole shift has reached its maximum at thin silica shells due to stronger localization of the quadrupole local field. The dipole peak continued to shift because the field extends further into the medium. A control nanoparticle suspension containing no silica was used to determine the shift due to ethanol only. From this, subtraction was done in Spectra Solve to determine the red shift in both the dipole and quadrupole peaks due to the condensation of the silica.

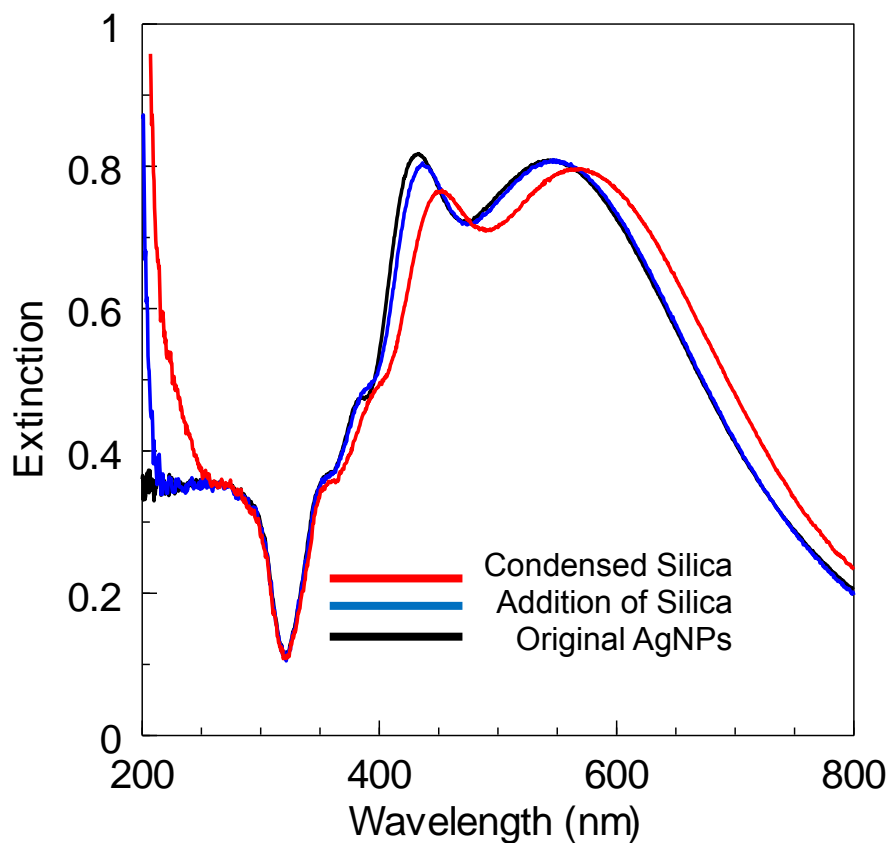


Figure 2.1 Shift in plasmon resonance due to the addition of a silica shell with arbitrary units for extinction. Black line is the original AgNP with the ultra-thin shell, blue is the addition of sodium silicate, and red is after condensation of silica via ethanol precipitation.

SEM images were taken of the original AgNPs and the thick silica shell AgNPs as a comparison (figure 2.2). On this particular instrument, the ultra-thin shell is not visible but the thick shell can be seen on the AgNP in figure 2.3.

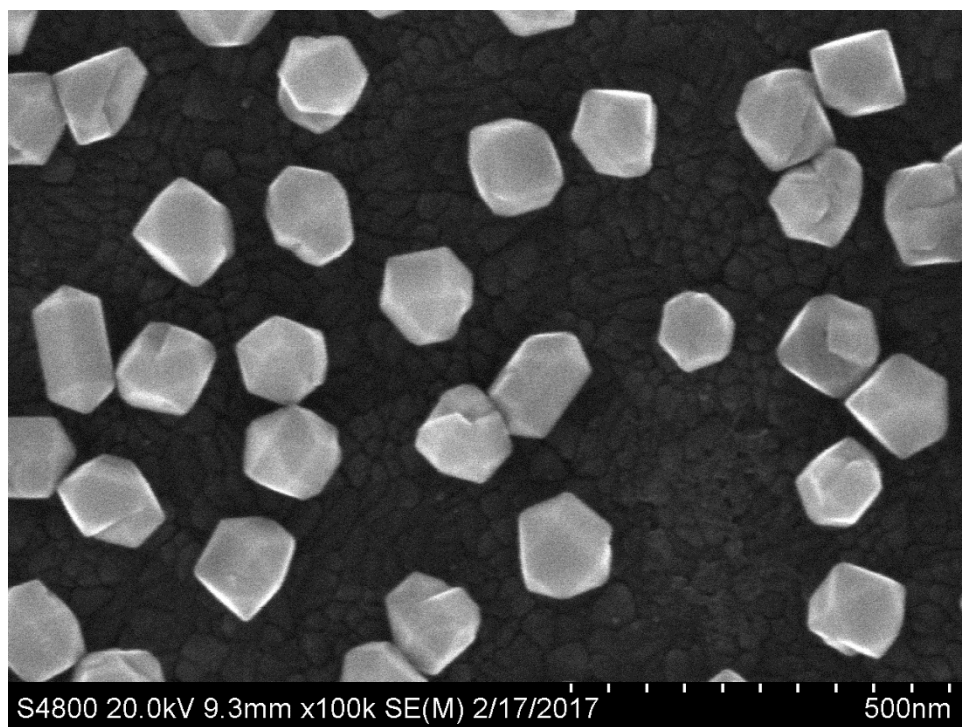


Figure 2.2 SEM image of the original AgNPs before ethanol precipitation of the silica shell on ITO glass modified with 0.25% PVP.

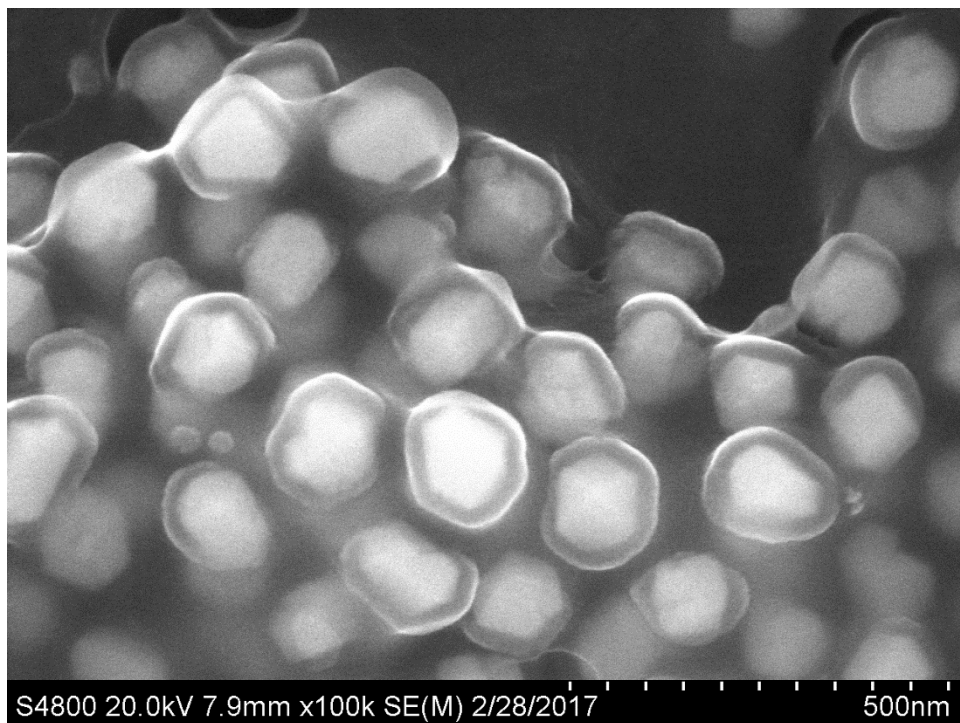


Figure 2.3 SEM image of AgNPs after the condensation of the silica shell on ITO glass modified with 0.25% PVP.

The silica shell, shown in figure 2.4, has a thickness of approximately 28nm  $\pm$  5nm. The thickness is consistent with all AgNPs in the solution. This simple method allows controlled thickness of a silica shell. The shell increases the stability of the AgNPs and prepares them for further surface modifications.

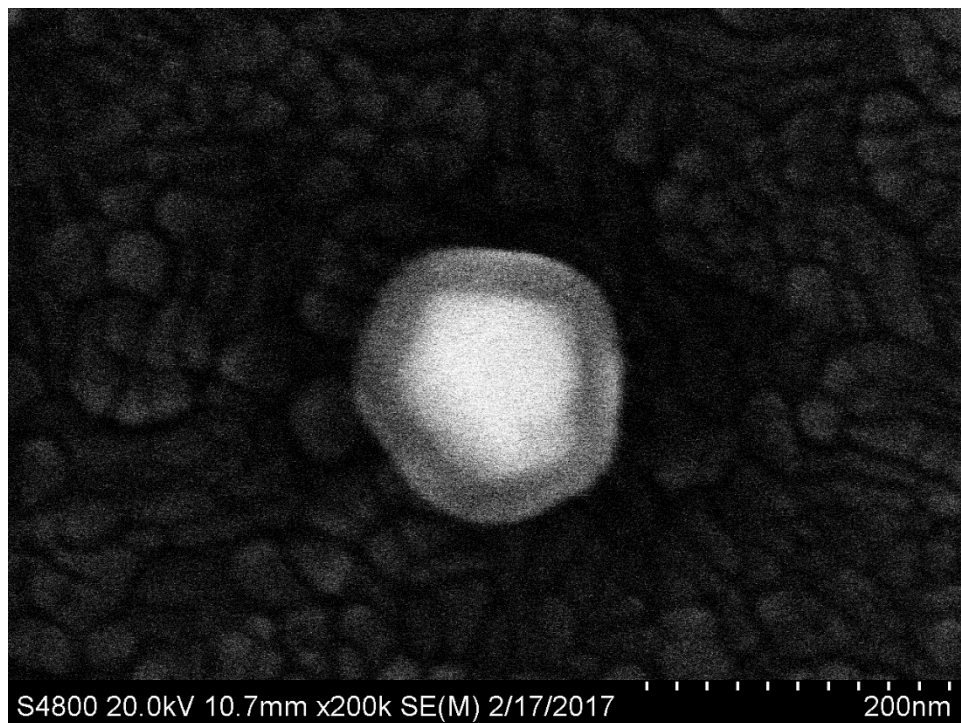


Figure 2.4 Representative SEM image of a AgNP with the thick silica shell. The particle is on ITO glass modified with 0.25% PVP.

In conclusion the thick silica shell were successfully synthesized around the AgNPs via ethanol precipitation. This silica shell allowed the synthesis of silver dimers by impregnating of silver ion followed by hydrogen reduction. It is expected that this approach can be developed into a general method for synthesizing oligomeric structures containing different nanoentities of different chemical nature.

# CHAPTER THREE

## SYNTHESIS OF ASYMMETRIC SILVER DIMERS AND OTHER OLIGOMERIC STRUCTURES

### Introduction

Dimers, trimers, and higher oligomeric structures have been desired for many different applications. They are considered multifunctional nanoentities with unique plasmon properties. The real challenge in oligomeric structures is not imagining possible applications but synthesizing these structures uniformly and in bulk. Many methods have used self-assembled monolayers which are not uniform or only a percentage of the nanoclusters contain dimers.<sup>11</sup> The method described here, is a simple way to make a homogeneous solution of dimers or other oligomeric structures at high concentrations with the possibility of making different compositions.

### Materials and Methods

Materials: Silver (I) oxide (99.99%) and Silver Sulfate (98%) were purchased from Alfa Aesar. Sodium Metasilicate ( $\text{SiO}_2$  44-47%) and 160000 MW Poly(4-vinylpyridine) (PVP) were purchased from Sigma-Aldrich. Ultra high purity hydrogen was purchased from Air Gas. Deionized water with a



normal resistivity of  $18\text{M}\Omega\cdot\text{cm}$  was obtained from a Millipore Milli-Q water purification system. USP/ACS grade absolute 200 proof ethanol was obtained from Aaper Alcohol & Chemical Company. Indium tin oxide (ITO) glass ( $8\text{-}12\Omega/\text{sq inch}$ ) was purchased from Sigma and Delta Technologies, LTD. Conductive Silver paint was purchased from PELCO®.

Instrumentation: A Shimadzu UV-2501 PC spectrometer was used to record all UV-vis spectra. A Hitachi SEM-4800 was used to take scanning electron microscopy (SEM) images. A Scintag 3100 PXRD with a Cu K $\alpha$  source was used to get powder X-ray diffraction patterns.

Methods: The thick silica shell AgNPs discussed in the previous chapter were used in the making of the AgNP dimers. 5 mL of a solution containing these particles were added to a 20 mL Teflon® reactor. The Teflon® reactor was used to eliminate contamination of silica from dissolved glass reactors. Then a solution of 10-100 $\mu\text{M}$   $\text{Ag}_2\text{SO}_4$  in 80% ethanol was added to the particles, giving a total volume of 10 mL. Recording of the spectral changes upon each addition to the thick silica shell particles was recorded using the UV-vis spectrometer. Once the solution was made, the reactor heated for 1.5 hours to reach  $73^\circ\text{C}$ . After the set temperature was

reached, hydrogen gas was turned on for 2-6 hours. The spectrum was recorded after hydrogen reduction using the UV-vis spectrometer. Procedure for SEM slides for these samples is as described in chapter two.

### Results and Discussion

As long as the AgNPs containing a thick silica shell were in 80% ethanol, the shell remained intact. The stability which the shell gave the AgNPs allowed them to undergo the hydrogen reduction reaction again without any aggregation occurring. The silver ions spontaneously go onto the surface of the thick silica shell AgNPs. Reduction of the silver ions into AgNPs made uniform suspension of small AgNPs attached to the large thick silica shell AgNPs. The structure of the cluster is dependent on the concentration of silver ions added to the colloidal suspension of thick silica shell AgNPs.

In figure 3.1, two to three major peaks can be seen in the UV-vis spectra of the oligomeric structures. These peaks are associated with certain modes which originate from the interaction between the plasmon resonances of each particle. With increasing amounts of  $\text{Ag}_2\text{SO}_4$  added to the reaction, the extinction at the 420nm peak increased. The increase indicates that adding more silver ions enhanced the plasmon resonance associated with this mode. As more silver ions are added, the spectrum

changes. This is due to the change in coupling of the plasmon resonances because of the change in the oligomeric structure. The addition of 10 $\mu$ M silver ions did not change the spectrum of the large AgNPs because the small particles did not affect the plasmon resonance of the large particles to an appreciable degree. As the concentration of silver ions increases, more particles with increased size are made. This changes the spectrum because plasmon resonance in both particles start to affect one another. The way in which the plasmon resonances couple gives rise to the addition of peaks and shifts in peaks in the spectrum.

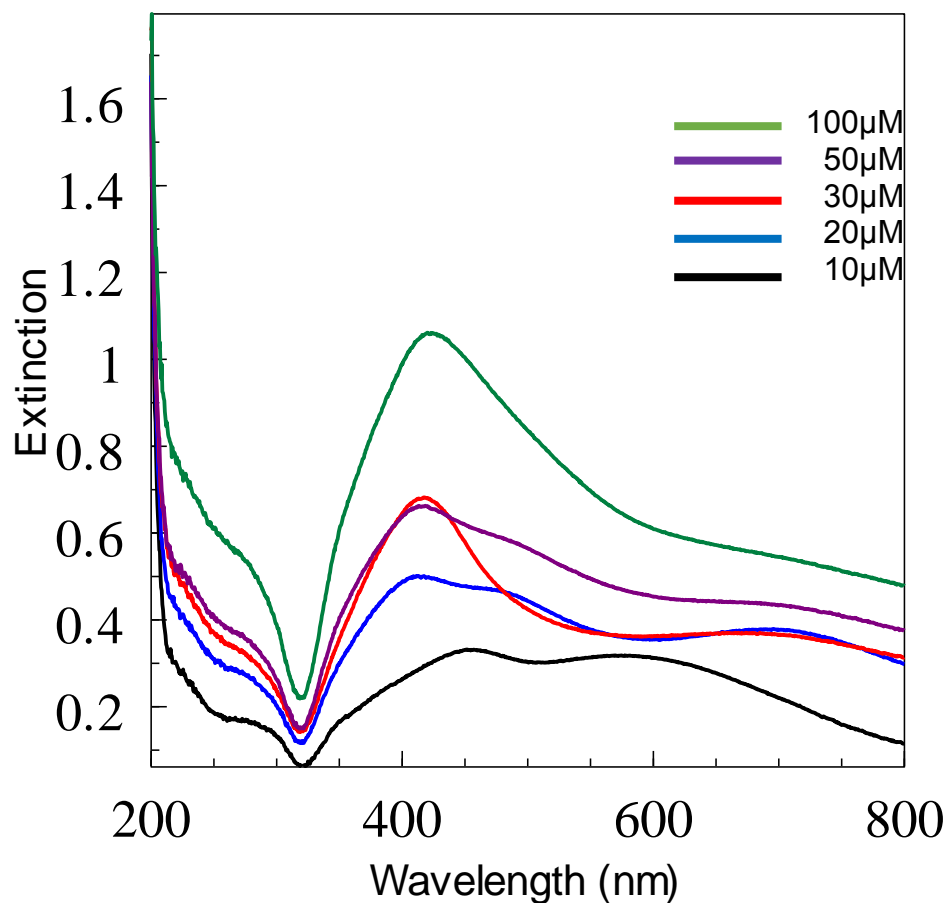


Figure 3.1 UV-vis spectra of different oligomeric structures after hydrogen reduction using different concentration of silver sulfate. Extinction has arbitrary units. Black line is 10 $\mu\text{M}$  addition of  $\text{Ag}_2\text{SO}_4$ , blue is 20 $\mu\text{M}$   $\text{Ag}_2\text{SO}_4$ , red is 30 $\mu\text{M}$   $\text{Ag}_2\text{SO}_4$ , purple is 50 $\mu\text{M}$  and green is 100 $\mu\text{M}$   $\text{Ag}_2\text{SO}_4$  addition.

Different concentrations of silver ions reduced on the surface of the large thick silica shell AgNPs produced different oligomeric structures as

can be seen in figure 3.5. The 30 $\mu$ M addition of silver ions created asymmetric dimers in a homogeneous suspension (figure 3.2). The UV-vis spectrum of these particles contains two major peaks, one peak at 420nm and the other at 680nm. These peaks correspond to the transverse and longitudinal modes of the plasmonic dimer.<sup>9,11,16</sup> The transverse mode is associated with the peak at 420nm which oscillates at a higher frequency than the longitudinal mode located at 680nm. The distance between the two peaks can be an indication of distance between the AgNPs but the complexity associated with dimer's plasmonic system increases exponentially with size and addition of silica. The predicted shape of the cluster is confirmed with SEM images of the asymmetric dimers.

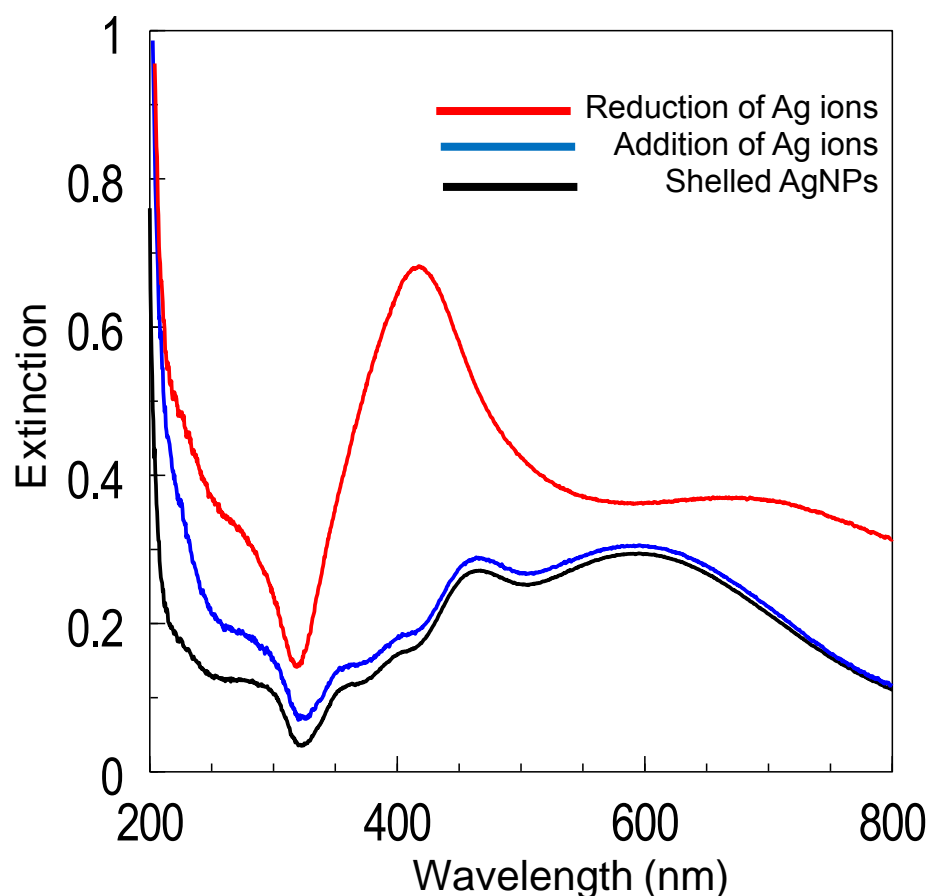


Figure 3.2 UV-vis spectra of the change in plasmon resonance of the thick silica shell AgNPs due to the addition of 30 $\mu$ M Ag<sub>2</sub>SO<sub>4</sub>. Extinction has arbitrary units. Black line is before addition of Ag<sub>2</sub>SO<sub>4</sub>, blue is after the addition of Ag<sub>2</sub>SO<sub>4</sub>, and red is after hydrogen reduction of the silver ions.

As shown in figure 3.3, the core AgNP including its thick silica shell is approximately 175nm in size with a smaller AgNP of approximately 50nm in size attached to it.

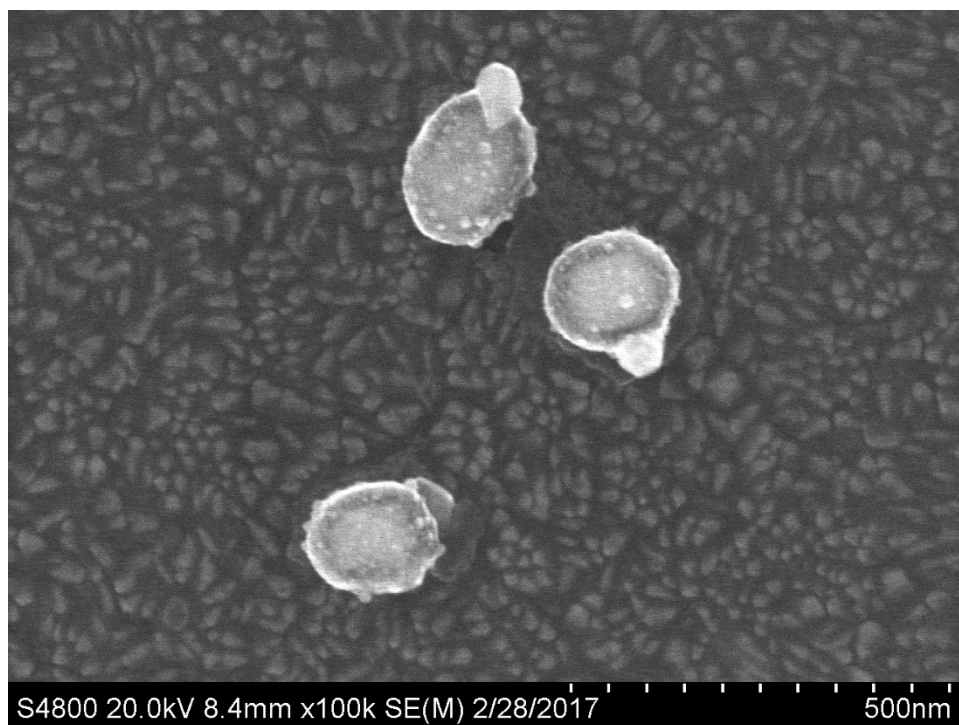


Figure 3.3 SEM image of silver dimers containing small AgNPs less than 10nm in size on ITO glass modified with 0.25% PVP.

Using this simple method of adding 30 $\mu$ M silver ions, silver dimers can be made uniformly in bulk, as shown in figure 3.4.

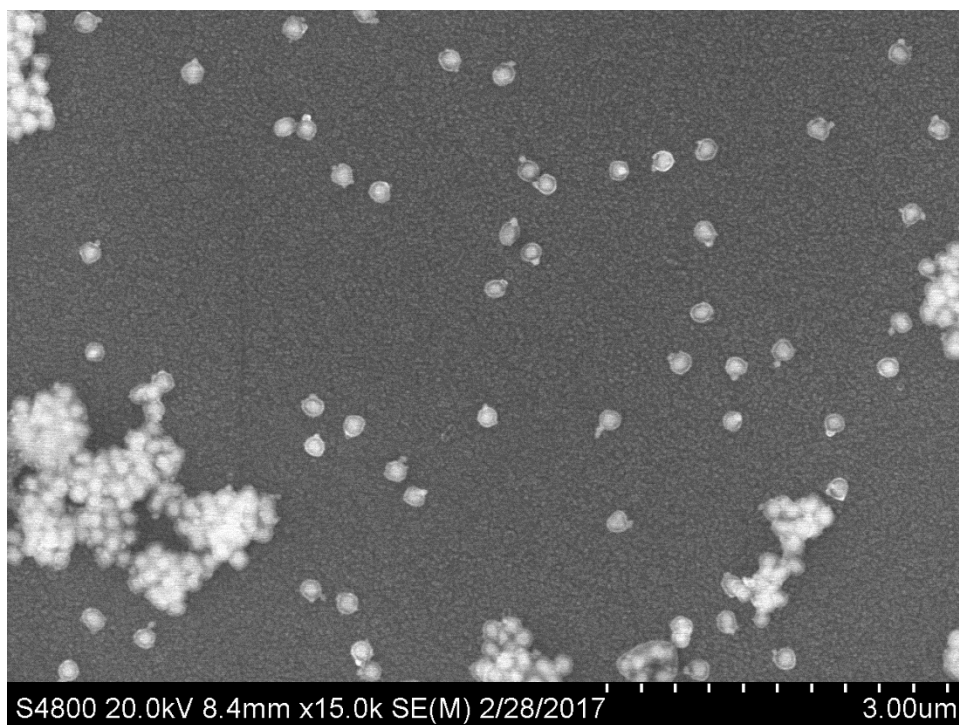


Figure 3.4 SEM image of silver dimers on ITO glass modified with 0.25% PVP.

While the asymmetric dimers are homogeneous, they still contain many AgNPs which are less than 10nm in size along with the approximately 50nm AgNPs. To make a dimer without small particles, more time was added to the hydrogen reduction reaction. With increasing time, the small particles did not undergo Ostwald ripening.<sup>17</sup> Ostwald ripening describes how small particle dissolve and redeposit on large particles because large particles are more energetically favorable. Creation of more small AgNPs is most likely due to the thick silica shell. The small particles get trapped in the



shell and cannot dissolve to recombine with other particles. This is evident in the time and increase in silver ion concentrations studies where more small AgNPs were made rather than the formation of a few large AgNPs on top of the large thick silica shell AgNPs. SEM images shown in figure 3.5 have different concentrations of silver ions or different times of hydrogen reduction reaction. Top left is 10 $\mu$ M silver ion addition, 2 hours of reduction, bottom left is 30 $\mu$ M silver ion addition, 2 hours of reduction. Then top right is 100 $\mu$ M silver ion addition, 2 hours of reduction. The bottom right is 30 $\mu$ M silver ion addition for 5 hours.

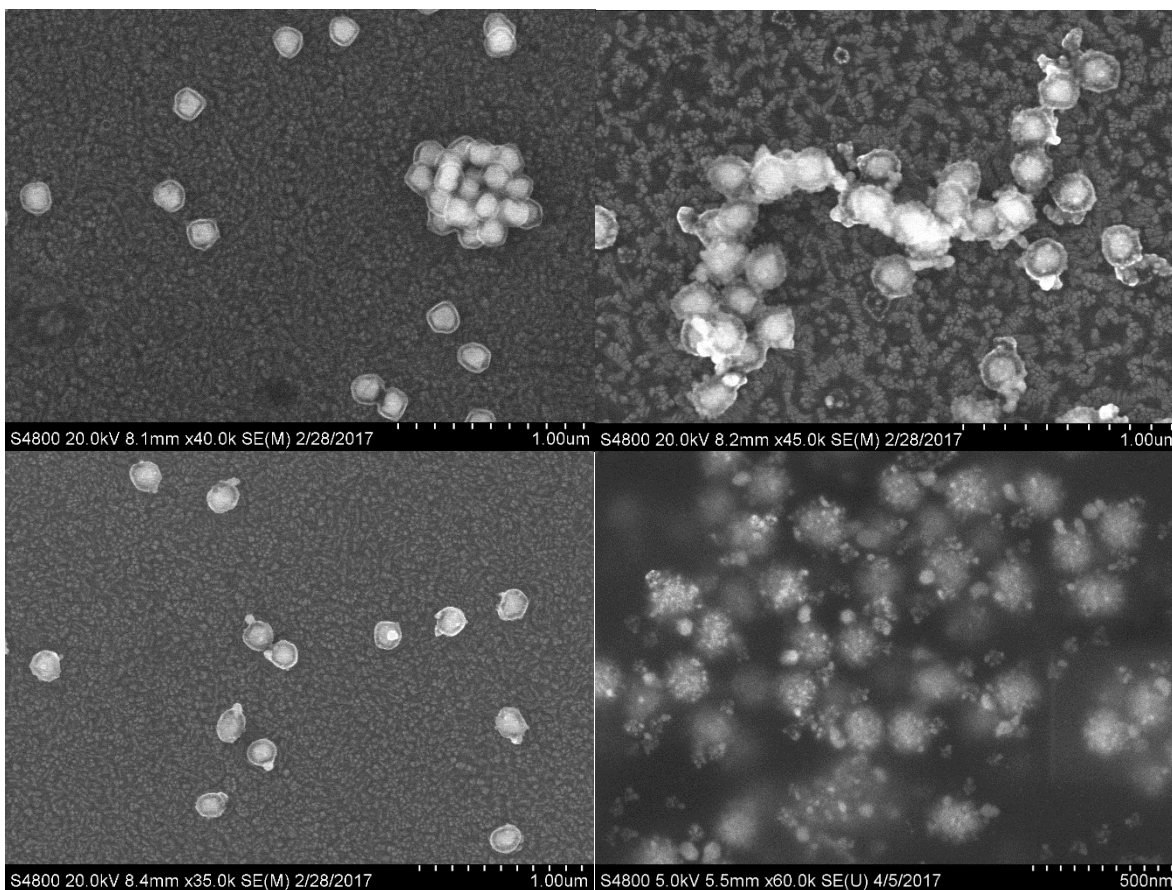


Figure 3.5 SEM images of silver AgNP clusters. Addition of 10µM Ag<sub>2</sub>SO<sub>4</sub> reduced for 2 hours onto the thick silica shell AgNPs (top left), addition of 30µM Ag<sub>2</sub>SO<sub>4</sub> reduced for 2 hours onto the thick silica shell AgNPs (bottom left), addition of 100µM Ag<sub>2</sub>SO<sub>4</sub> reduced for 2 hours onto the thick silica shell AgNPs (top right), and addition of 30µM Ag<sub>2</sub>SO<sub>4</sub> reduced for 5 hours (bottom right).

As the reduction time or concentration of silver ions increases, the oligomeric structure changes. More particles are made in the shell rather than a perfect dimer containing only two AgNPs. The addition of more AgNPs upon increasing time to the 30µM addition of silver ions indicates

that the reaction had not gone to completion at 2 hours. The dimer made at 2 hours is an intermediate stage in the reaction process where completion is considered to be the reduction of all silver ions.

Addition of silver ions for reduction to these thick silica shell AgNPs is only the beginning stages of these multifunctional nanoentities. The dimers made here are a step in the right direction to making a simple scaffold for further modification.

## CHAPTER FOUR

### ROUNDING OF SILVER NANOPARTICLES DUE TO DISSOLUTION OF SILVER IONS

#### Introduction

AgNPs are in the crystalline form because this phase is the lowest energy phase. The lowest crystalline form contains large facets which are stable and slow to react. When the large facets of the AgNPs start to dissolve, smaller facets are formed. These facets are faster at reacting because they are not as stable as the large facets. The dissolution of the surface of the AgNPs creates these small faces until the particle appears round. The AgNP is still crystalline but the particle has taken on a more reactive crystalline form. The increase in reactivity could give these rounded AgNPs some unique properties including faster reactivity, increased catalytic activity, and increased scattering.<sup>11</sup>

#### Materials and Methods

Materials: Silver (I) oxide (99.99%) was purchased from Alfa Aesar. Sodium Metasilicate (SiO<sub>2</sub> 44-47%) and 160000 MW Poly(4-vinylpyridine) (PVP) were purchased from Sigma-Aldrich. Ultra high purity hydrogen was purchased from Air Gas. Deionized water with a normal resistivity of

18M $\Omega$ ·cm was obtained from a Millipore Milli-Q water purification system. USP/ACS grade absolute 200 proof ethanol was obtained from Aaper Alcohol & Chemical Company. Indium tin oxide (ITO) glass (8-12 $\Omega$ /sq inch) was purchased from Sigma and Delta Technologies, LTD. Conductive Silver paint was purchased from PELCO®.

Instrumentation: A Shimadzu UV-2501 PC spectrometer was used to record all UV-vis spectra. A Hitachi SEM-4800 was used to take scanning electron microscopy (SEM) images. A Rigaku Ultima IV diffractometer was used to collect the X-ray diffraction pattern in the Bragg-Brentano geometry using Cu K $\alpha$  radiation ( $\lambda=1.5406$  Å, sealed glass tube). The step size was 0.02 degrees in 2 $\Theta$  degree ranging between 10 and 90 degrees with a scan rate of 1.500 deg./min. The sample holder was a silicon zero background holder.

Methods: AgNPs were made using the ultra-thin shell method described in chapter 2. These particles were filtered to remove excess Ag<sub>2</sub>O. The nylon membrane had a pore size of 0.22 microns. At 1,000 rpm, the AgNPs were spun down and the supernant was removed to concentrate the particles. To cause the rounding of the AgNPs, an aliquot was taken and diluted with DI water between 25-100%. Depending on the percent of dilution and the thickness of the ultra-thin silica shell, the particles took

between 4-24 hours to start rounding. This rounding was monitored with a UV-vis spectrometer as a blue shift in the spectrum.

### Results and Discussion

The observation of the AgNPs rounding was first noticed as a color change. AgNPs which were green in color appeared white after 24 hours. As shown in figure 4.1, the UV-vis spectrum was blue shifted and the shoulders between the 320nm dip and quadrupole were now smooth. Since blue shifts in the UV-vis spectra indicate that particles are decreasing in size, a hypothesis was made that silver was being lost from the particle and going back into solution.

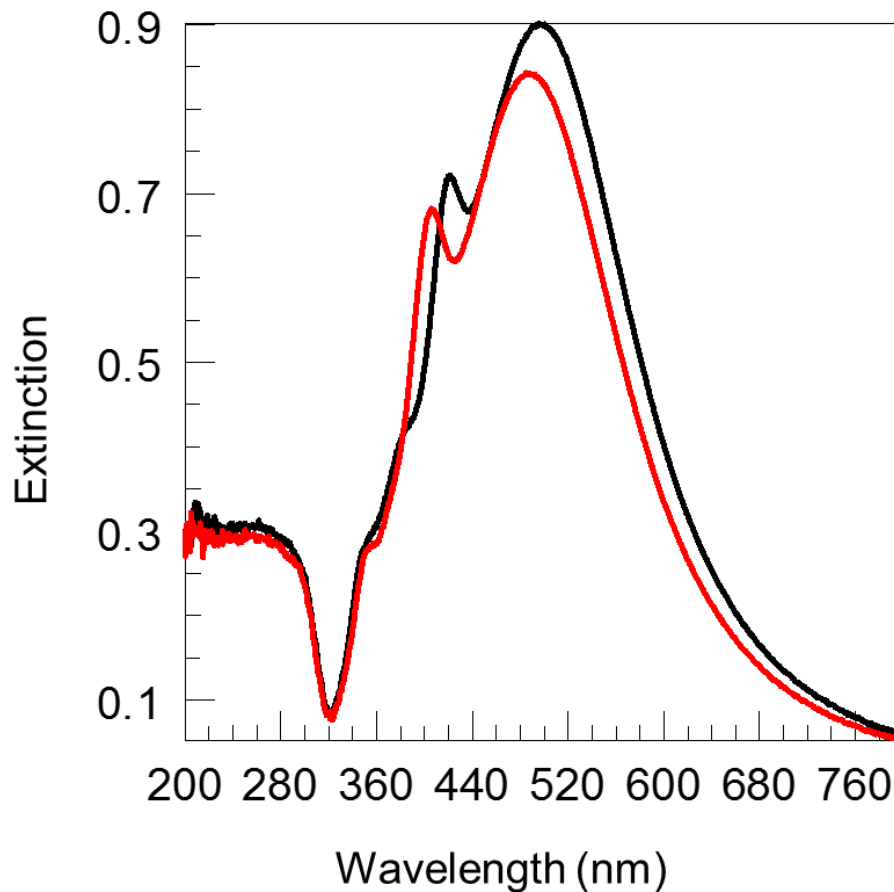


Figure 4.1 UV-vis spectra of the shift in the plasmon resonance of AgNPs due to shape change with arbitrary units for extinction. The black line is AgNPs diluted 100 times. The red line is the same AgNPs after 13 days.

To test this hypothesis, the AgNPs were spun down and the supernatant was separated from the particles. Then sodium borohydride was added to the clear supernatant. Sodium borohydride is used to reduce

silver, creating small AgNPs as hydrogen is released. The color change confirmed our suspicion that silver ions were leaving the surface of the nanoparticle. This explained the blue shift in the plasmon resonance but not the smoothing of the shoulders. According to Rycenga *et al*, the shoulders on the quadrupole peak of the UV-vis spectrum has indicated the corners of the AgNPs.<sup>11</sup> A typical AgNP has a polyhedral structure sharp corners at the ends of the crystal. These corners are where we believe the silver is coming off of the particle. As these sharp corner facets smooth out, so do the shoulders on the UV-vis spectrum. The smoothing of the corners gives the particles a spherical shape as compared to the polyhedral shape which they initially exhibited. To make sure that this change in the particles was just a shape change and not a phase change, Powder X-Ray diffraction (PXRD) was done on the original AgNPs with no change in the UV-vis spectrum and the whitening AgNPs, shown in figure 4.2. There was no shift in the peaks of the samples therefore the crystallinity of the particles remained intact and no phase change was observed.



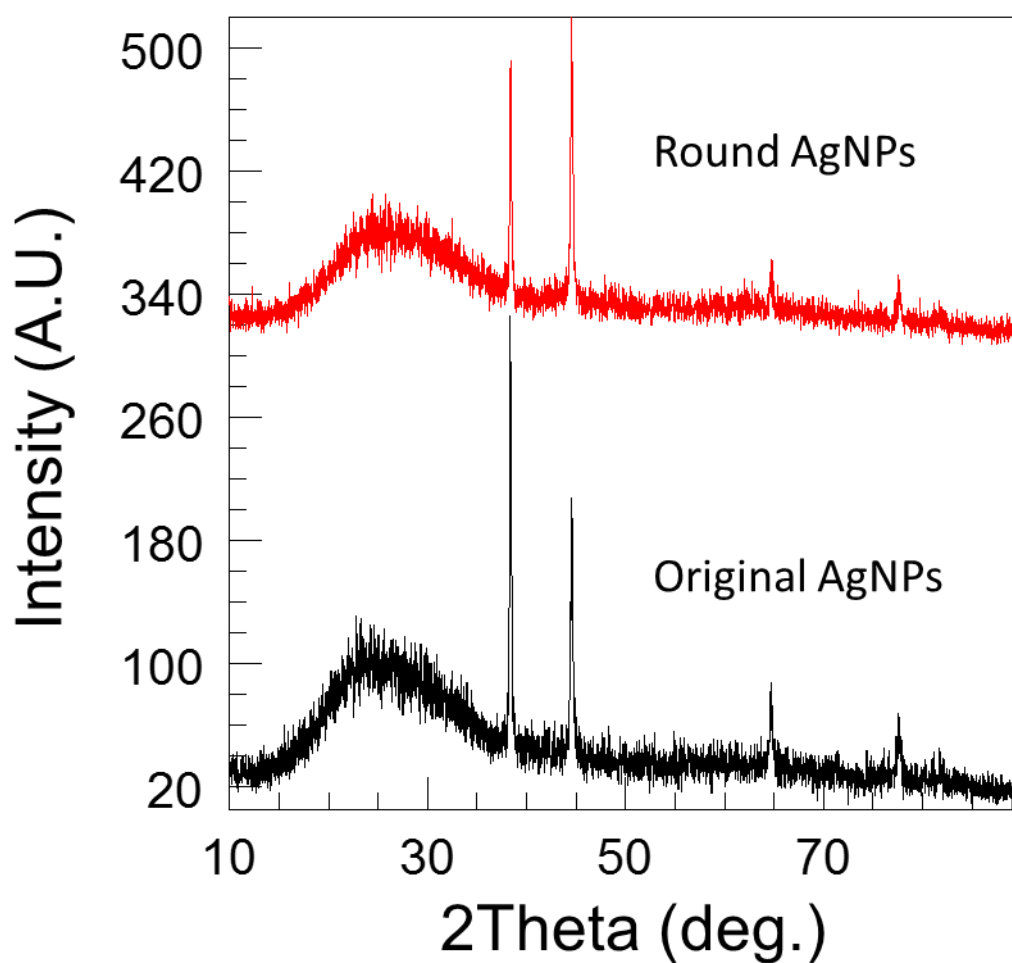


Figure 4.2 XRD of the original AgNPs (black curve), and XRD of the whitened AgNPs (red curve) with a scan speed of 1.000 deg./min from 10.0000 – 90.0000 deg.

To confirm the shape change of the AgNPs, SEM imaging was done on both sets of particles (figure 4.3). The original particles have their typical polyhedral shape while the whitened particles appear to be spherical. The

large facets of the polyhedral were gone and small facets took their place. In crystals, the smaller facets are the most reactive. They are fast growing and are the active sites of the crystal. Because the white AgNPs are made of small faces, these particles could be considered a more reactive crystalline form.

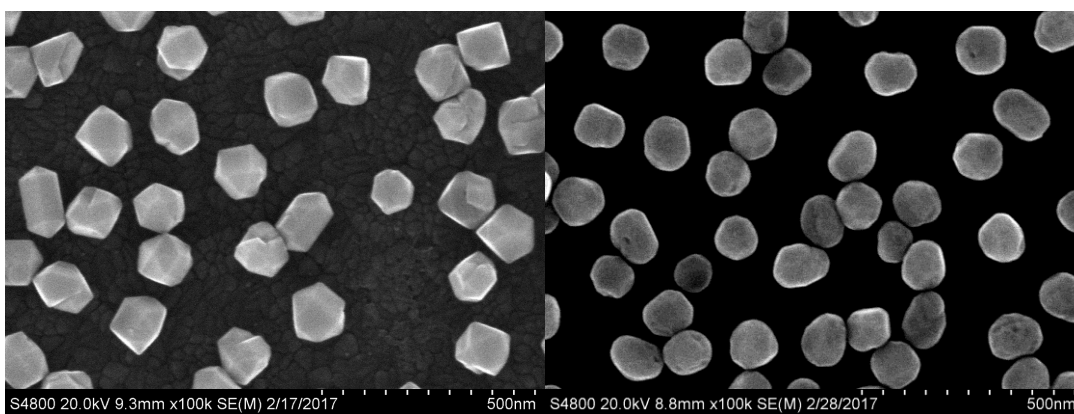


Figure 4.3 SEM images of original AgNPs (left), UTSS not shown and rounded AgNPs after 100 time dilution (right) both on ITO glass modified with 0.25% PVP.

Figure 4.4 shows another image of the rounded AgNPs. In this image, the large facets are gone leaving a smooth appearance of the particles.

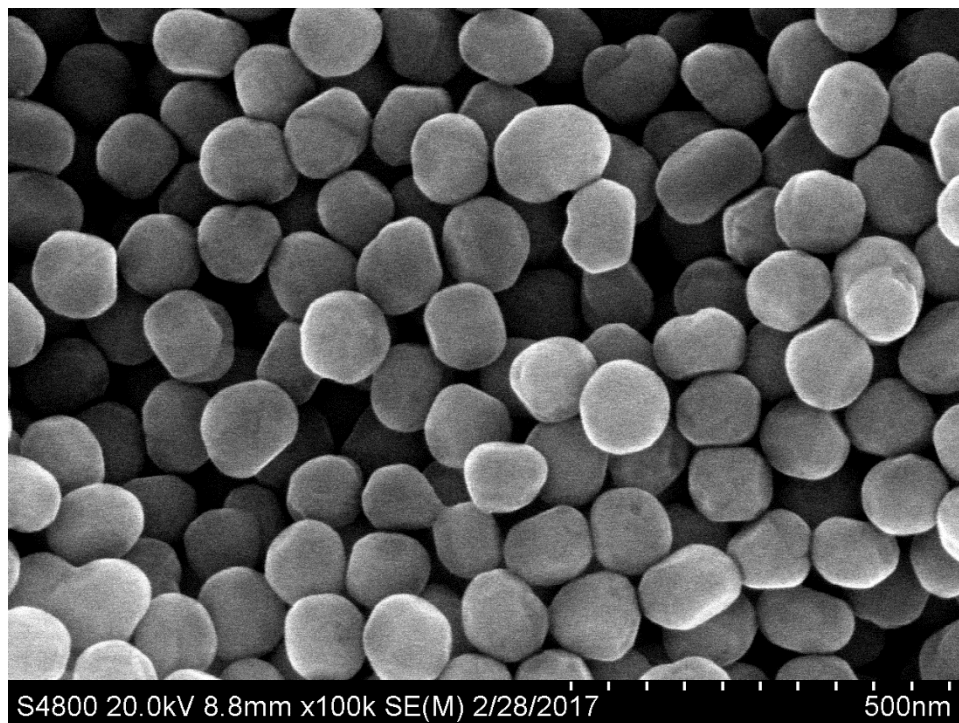


Figure 4.4 SEM image of rounded AgNPs on ITO glass modified with 0.25% PVP.

To monitor the shaping changes of the AgNPs, an investigation of the blue shift over time was monitored using a UV-vis spectrometer. Figure 4.5 shows the blue shift in the plasmon resonance of the AgNPs over time. The shift decreases with increasing time and eventually stops shifting. This could be an indication of an equilibrium occurring. The stable particles are in a solution of saturated  $\text{Ag}_2\text{O}$  but with the addition of DI water, the solution is no longer saturated with  $\text{Ag}_2\text{O}$ . The etching of the AgNP surface could be

caused by this shift in the equilibrium. Once the equilibrium is restored, the particles stop blue shifting.

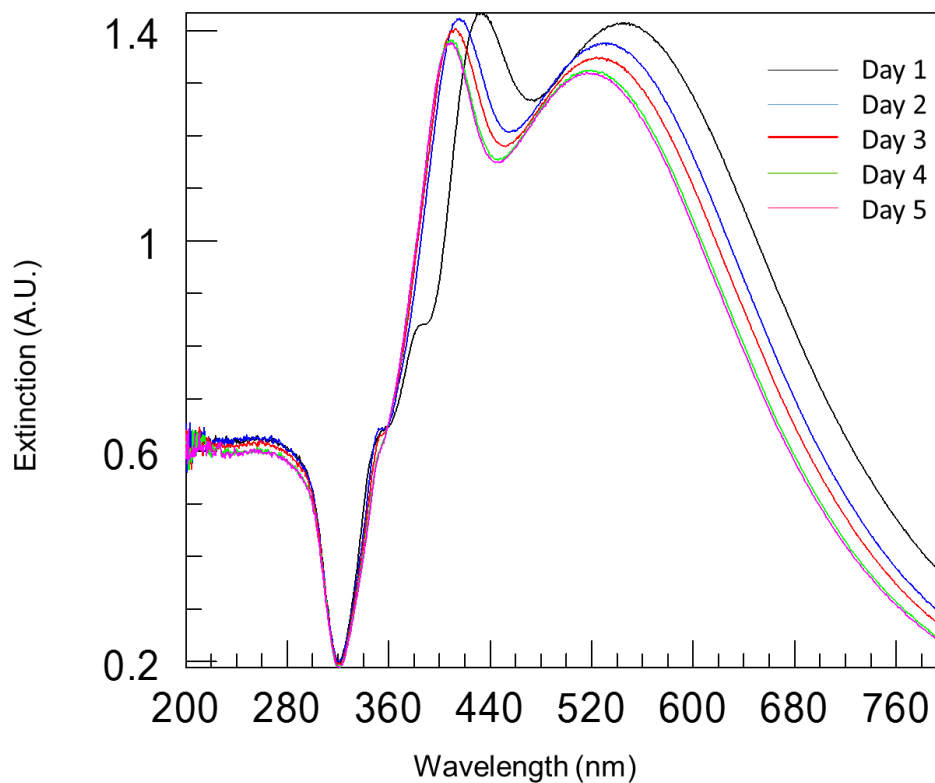


Figure 4.5 UV-vis spectrum of shift in time in 100x diluted AgNPs.

All of the previous data shown on the rounded AgNPs were diluted 100x with DI water. To test if the dilution was a factor in the observed rounding of the AgNPs, different dilutions ranging from 25-100x was monitored. Figure 4.6 shows a blue shift in all of the diluted samples corresponding to rounding of the AgNPs.

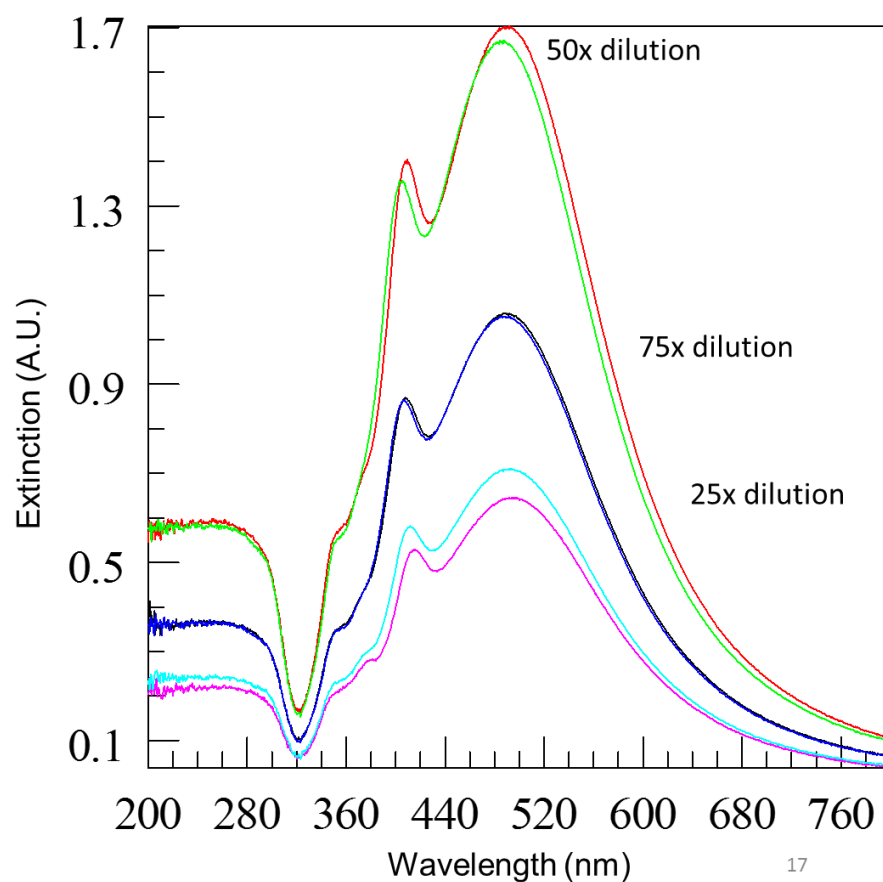


Figure 4.6 UV-vis spectrum of different dilutions of AgNPs with DI water 1 day apart. The 25x dilution has been further diluted by 1/3 for data analysis.

While the cause of the shape change in the AgNPs is unknown at this time, evidence of a shift in the equilibrium between silver on the surface of the particle and silver ions in solution, seems to play an important role.

## CHAPTER FIVE

### CONCLUSIONS AND FUTURE WORK

The presented work is concerned with the modification of silver nanoparticles with silica via ethanol precipitation. The silica shell served two purposes; stabilization of AgNPs against aggregation specifically when various surface modifications when added as well as providing a scaffold for further modification with the impregnation of silver ion. The later was accomplished via hydrogen reduction via impregnation of silver ion around the silver core. The concentration of the silver ions as well as the hydrogen reduction time had a large effect on the resultant oligomeric structures. Depending upon the reaction conditions, the oligomeric structures ranged from pure silver dimers composed a large silver core and a smaller silver particle attached to the shell to small silver particles uniformly trapped in the shell. More extensive studies needs to be performed to control the formation of pure dimers and small particles throughout the shell. Conceivably the shell needs to be thick enough to completely cover the particle and allow impregnation of the silver ions but thin enough that the small particles are not trapped in the shell and can coalesce into a larger particle thereby forming a dimer. The impregnation of AgNPs is not limited to silver ions. In this work silver ions were used to prove the concept for how

various oligomeric nanostructures can be made consisting of nanoparticles with different chemical origin. Such oligomeric nanostructures can be multifunctional and provide endless possibilities for applications. The method developed here provides a general strategy for synthesizing such structures.

The etching of crystalline AgNPs resulting in the formation of rounded nanoparticles that was also observed requires comprehensive investigation. Wide change in experimental conditions should be undertaken as well as more comprehensive characterization are required for better understanding and control of the etching process. Due to the formation of additional crystal facets after nanoparticle etching these particles are expected to have a more reactive surface and may find applications in Surface Enhanced Raman Spectroscopy (SERS) and catalysis. The lack of fundamental understanding of the etching process as well as the potential exciting applications make this research highly important to pursue.

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